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Photoluminescence of a Te^{4+} center in zinc borate glass

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Photoluminescent (PL) properties related to Te^{4+} species in zinc borate glasses are examined. Broad emission was observed by the excitation of the PL excitation peak of Te^{4+} present at the optical absorption edge. The emission intensity of Te^{4+} in $5\text{TeO}_2\text{--}50\text{ZnO--}45\text{B}_2\text{O}_3$ glass was thermally quenched in a temperature region over 100 K, suggesting that concentration quenching preferentially occurred. The lifetime of the emission was approximately 2.5 μs , which is characteristic of relaxation from the triplet excitation state of an ns^2 -type center. © 2013 Optical Society of America

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The emission properties of atomic or ionic emission centers have attracted attention not only from the scientific community but also from industry. ns^2 -type ions ($n = 4, 5, 6$) are ions exhibiting an ns^2 electron configuration in the ground state and an ns^1np^1 configuration in the excited state [1]. Because of the parity-allowed transition, ns^2 -type emission centers such as Sn^{2+} [2,3], Sb^{3+} [4,5], Tl^+ [6], Pb^{2+} [7], and Bi^{3+} [8] cations can exhibit strong emission intensities. On the other hand, because these emission centers possess electrons in the outermost shell, the emission properties are strongly affected by the coordination field. Upon excitation by UV light broad-band emission, whose lifetime is usually on the microsecond scale, is observed. For example, Sb^{3+} , Mn^{2+} codoped calcium halophosphate crystals have been used as phosphors for practical white fluorescent lamps [1,4].

However, the number of ns^2 -type emission centers previously reported is limited, even though several cations or atoms have the same electron configuration. It is notable that there are only a few reports concerning the emission of Te^{4+} cations in alkali halides [9–13] and there is only one report on the luminescence of Te^{4+} in oxide crystals [13]. In addition, the reported emission in oxide crystals was measured at a liquid helium temperature of ~ 8 K rather than at room temperature because of the low emission intensity [13]. Moreover, luminescence of Te^{4+} in an amorphous material has not been reported so far. On the other hand, it is expected that amorphous glass is a suitable host for metastable species such as Te^{4+} because of the wide site distribution. However, Te^{4+} has so far not been considered as an emission center in conventional glass science, although TeO_2 has attracted much attention as a good host for laser media exhibiting low-phonon energy and a wide transmission window in the IR region. Therefore, it is worthwhile to demonstrate the emission of Te^{4+} species in an oxide glass.

Because Te cations are easily reduced into Te metal during melting at high temperatures (over 1200°C), a stable oxide glass system prepared at a lower temperature is preferable. In the present study, we selected zinc borate glass, $50\text{ZnO--}50\text{B}_2\text{O}_3$, as a host glass because it possesses a relatively low melting temperature ($\sim 1100^\circ\text{C}$) and good chemical durability. Because the chemical

formula $50\text{ZnO--}50\text{B}_2\text{O}_3$ is the stoichiometric composition of the ZnB_2O_4 crystalline phase, which has been used as a host material for phosphor [14], it is expected that the borate glass would be a candidate for a host matrix. In contrast to Sn^{2+} centers, which can be doped in phosphate glasses [15–20], Te^{4+} centers cannot be introduced in a phosphate glass system because a reduction reaction of Te^{4+} into Te metal particles occurs during melting [21]. Hence, we selected the borate system as a host glass for Te^{4+} centers, whose emission properties have not been reported yet. The aim of the study is to demonstrate the photoluminescence (PL) properties of a Te^{4+} emission center in a borate glass.

The oxide glasses were prepared by a conventional melt quenching method in air using a platinum crucible. TeO_2 (99.999%), ZnO (99.99%), and B_2O_3 (99.99%) were mixed and then melted at 1100°C for 30 min in air. The nominal chemical composition of the glass was $x\text{TeO}_2\text{--}50\text{ZnO--}(50-x)\text{B}_2\text{O}_3$ (mol. %) and TeO_2 was added as a substituent of B_2O_3 . The glass melt was quenched on a stainless plate kept at 200°C , and the obtained glasses were annealed at the glass transition temperature T_g for 1 h. The samples were then mechanically polished to obtain a mirror surface. The value of T_g was determined by differential thermal analysis (DTA) operated at a heating rate of 10 K/min using TG8120 (Rigaku). The PL and PL excitation (PLE) spectra were measured at room temperature using an 850 fluorescence spectrophotometer (Hitachi). The absorption spectra were measured at room temperature using a U3500 spectrophotometer (Hitachi). The PL dynamics were also evaluated using a streak camera (Hamamatsu Photonics, Japan) and a monochromator (Hamamatsu Photonics, Japan). The light source used for photoexcitation was an optical parametric amplifier system based on a regenerative amplified mode-locked Ti:sapphire laser (Spectra Physics, USA) with a pulse duration of 150 fs and a repetition rate of 1 kHz. The photon energy was 4.96 eV, which corresponded to the peak energy of these PLE spectra. The PL spectra at different temperatures were also measured in the 8–350 K region using the same Ti-sapphire laser.

The obtained $x\text{TeO}_2\text{--}50\text{ZnO--}(50-x)\text{B}_2\text{O}_3$ glasses were transparent with no precipitation of metal nanoparticles. Figure 1 shows the absorption spectra of the

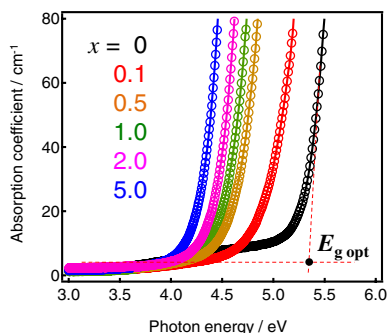


Fig. 1. Optical absorption spectra of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses at room temperature.

$x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses ($x = 0, 0.1, 0.5, 1.0, 2.0$, and 5.0). Per a previous report [15], we introduced an optical band edge, E_{gopt} , that was determined by extrapolation of the linear portion of the absorption coefficient. Although the value obtained is different from that using a conventional E_{gopt} calculated from the optical band gap of the host matrix, we use this value to discuss a relationship between the absorption properties and the emission properties of the Te^{4+} center (impurity). The value of E_{gopt} decreases with increasing TeO_2 amount, which is also observed in Sn^{2+} - and Sb^{3+} -doped oxide glasses [14–19,22]. The detailed relationship between the amount of TeO_2 and E_{gopt} is shown later in this Letter (see Fig. 4).

Figure 2 shows the PL and PLE spectra of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses ($x = 0.1, 1.0$, and 5.0). In the case of a glass containing a low amount of TeO_2 ($x = 0.1$), two emission bands are observed. The higher emission band at 3.5 eV can be assigned to the Zn-O charge transfer transition because the emission is observed in the undoped zinc borate glass. The lower emission band, which is shown using a dashed line, exhibits a broad emission whose peak energy and half-width at half-maximum (HWHM) are approximately 2.7 and 1.2 eV, respectively. The large HWHM of the PL emission, which is independent of the TeO_2 amount, is characteristic of an ns^2 -type emission center. The PLE peak energies redshifted with increasing TeO_2 amount, which corresponds to the energy shift of the absorption edge (see Fig. 1). The PLE band located at the optical absorption edge, E_{gopt} , is also characteristic of oxide glass containing ns^2 -type emission centers [14–19]. In the samples containing higher TeO_2 contents, the emission intensity

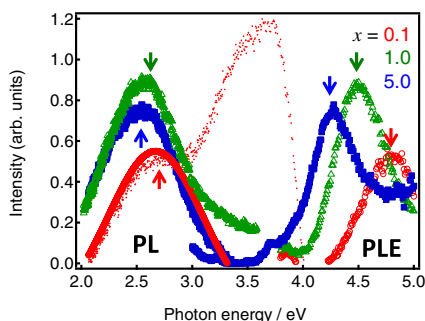


Fig. 2. PL and PLE spectra of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses at room temperature.

due to Zn-O decreases, which indicates that incident light is absorbed strongly by the Te^{4+} emission center, preventing absorption by the host matrix. The emission intensity of Te^{4+} showed the maximum value at a concentration of 1.0 mol. %, and concentration quenching was observed in the higher TeO_2 -containing samples.

Figure 3(a) shows the PL spectra of the 5 TeO_2 -50ZnO-45 B_2O_3 glass at different temperatures by the excitation of a wavelength-tunable femtosecond Ti:sapphire laser system (4.68 eV) with an excitation density of 0.5 W/cm². The emission intensity decreases with increasing temperature, and the peak position is slightly redshifted. This phenomenon is similar to that previously reported of Te^{4+} centers in phosphate crystals [13]. Figure 3(b) shows the change in the spectrally integrated PL intensity as a function of the inverse temperature, T^{-1} . We find that there are at least two activation energies of this emission and that significant thermal quenching is observed at temperatures over 100 K. The activation energies of the higher and lower temperature regions are 86.7 and 0.07 meV, respectively. As shown in Fig. 2, the PLE spectrum consists of at least two bands that are close together, and it is observed that the two activation energies may be due to these two excitation bands. It is also suggested that concentration quenching occurs at temperatures over 100 K because the concentration of Te cations (5 mol. %) is much higher than that of an emission center in a conventional phosphor.

Figure 4 shows the TeO_2 concentration dependence of the optical properties, i.e., the peak energies of the PL-PLE bands and the E_{gopt} of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses. These values were measured at room temperature. The values of the Stokes shift that correspond to the peak energy difference between the PLE

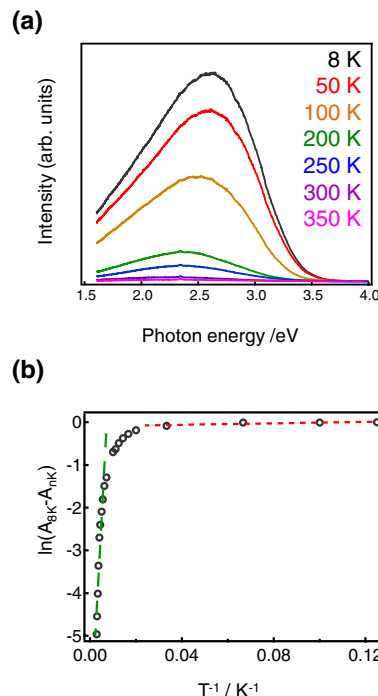


Fig. 3. (a) PL spectra of the 5 TeO_2 -50ZnO-45 B_2O_3 glass at different temperatures and (b) spectrally integrated PL intensity as a function of the inverse temperature, T^{-1} .

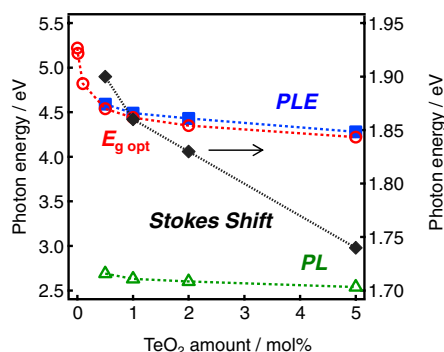


Fig. 4. Composition dependence of the peak energies of the PL and PLE bands and the Stokes shift of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses. The values of $E_{\text{g opt}}$ are also shown.

and PL bands are also shown. With an increasing amount of TeO_2 , both the excitation and emission peaks redshift, whereas the Stokes shift decreases. The figure also shows that there is a strong correlation between the PLE peak and the $E_{\text{g opt}}$. The Stokes shift of Te^{4+} in the present borate glasses is comparable to that in the previously reported zirconium phosphate crystal [13], indicating that the Stokes shift of Te^{4+} is mainly affected by the phosphate unit of the host matrix, not by the randomness of the matrix.

Figures 5(a)–5(d) show the PL–PLE contour plots of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses using an intensity axis on a linear scale. In each figure, the photon energy of excitation is plotted on the y axis and that of emission on the x axis, and the emission intensity axis is shown on an identical linear scale using colors. The 50ZnO-50 B_2O_3 glass [Fig. 5(a)] shows emission due to the Zn–O charge transfer transition. In the case of the 0.1Te sample [Fig. 5(b)], the emissions of both Te^{4+} (circled region) and Zn–O are observed. The emission peak and the excitation peak redshifted with increasing amounts of TeO_2 , as shown in Fig. 4. Although the emission intensity of

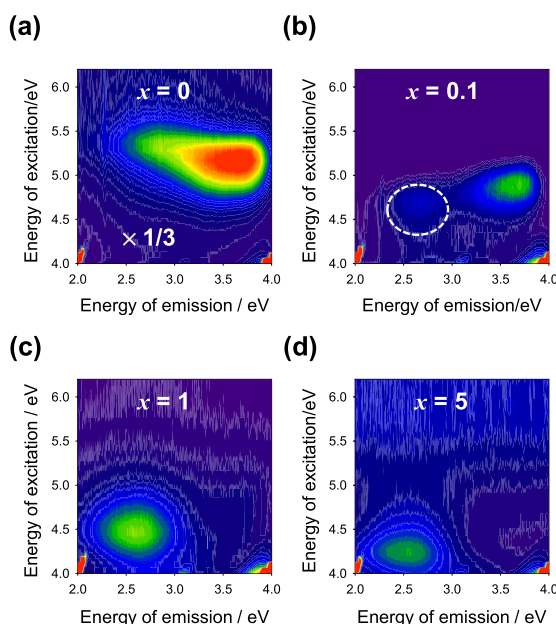


Fig. 5. PL and PLE contour plots of the $x\text{TeO}_2$ -50ZnO-(50- x) B_2O_3 glasses at room temperature.

Te^{4+} is weaker than that of the host matrix, the observed emission is due to Te^{4+} , which is difficult to observe in an amorphous matrix at room temperature.

In order to examine the emission decay, the streak image of the glass was measured. Figures 6(a) and 6(b) show a streak image of the 1 TeO_2 -50ZnO-49 B_2O_3 glass with irradiation of 250 nm as the light source and the emission decay curve calculated from the integral of the photon number in the 2.4–3.2 eV region, respectively. The streak image suggests that (1) the emission decay is on a microsecond scale, which is classified as triplet-singlet relaxation from the viewpoint of the timescale, and (2) that nonexponential decay with a peak shift toward lower photon energies occurs. This emission property is also observed in Sn^{2+} -doped zinc phosphate glass phosphors [23]. Therefore, the obtained TeO_2 -doped glass phosphor exhibited emission properties similar to that of conventional emission centers. Because the decay constant, $\tau_{1/e}$, of the Te^{4+} center is 2.5 μs , which is shorter than that of Sn^{2+} or Sb^{3+} [22], the decay constants of these $5s^2$ emission centers become shorter with increasing atomic number. The obtained results also suggest that TeO_2 glass containing higher amounts of Te^{4+} shows no emission because of concentration quenching. Actually, it was demonstrated that TeO_2 -based glass containing more than 30 mol. % Te^{4+} showed no emission [20], although the threshold depending on the chemical composition of the glass has not been clarified.

On the other hand, PL of Te species has not been fully clarified yet. It was reported that the Te^{2-} ion in $\text{ZnSe}_{1-x}\text{Te}_x$ also exhibited PL at liquid helium temperature [24]. Although the valence of the Te ion of the previous paper is different from that of the present case, they observed broad emission in the range of 2.1–2.8 eV resulting from exciton recombination of Te pairs or clusters. The report suggests that the redshift of the PLE band by increments in concentration of the present results may be due to the formation of clusters. Further study is needed for understanding the basic science to improve the performance.

In summary, we have examined the emission properties of Te^{4+} -containing zinc borate glass. In the 5 TeO_2 -55ZnO-45 B_2O_3 glass, emission quenching was observed at temperatures over 100 K, suggesting that concentration quenching occurred. Both the excitation energy and the optical absorption edge redshifted with increasing amounts of TeO_2 , whereas the emission peak

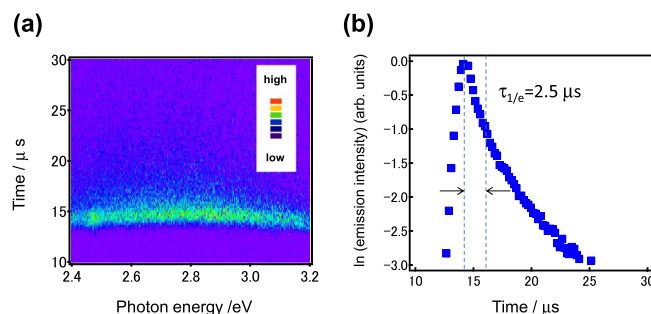


Fig. 6. (a) Streak image of the 1 TeO_2 -50ZnO-49 B_2O_3 glass with irradiation of 250 nm and (b) an emission decay curve of the 1 TeO_2 -50ZnO-49 B_2O_3 glass calculated by the integral of the photon number in the 2.4–3.2 eV region.

was also slightly redshifted. The decay constant $\tau_{1/e}$ was approximately 2.5 μ s, which suggests a spin-forbidden triplet-singlet transition of the Te^{4+} center. From these characteristics, we have demonstrated that Te^{4+} cations possess emission properties that are characteristic of ns^2 -type emission centers in oxide glasses.

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